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# Analysis of volume expansion with temperature for some alkali halides along isobars at high pressures

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**Abstract** : In the present study, we have determined the volume expansion with temperature in case of LiF, NaF and CsCl crystals along isobars. A formulation has been developed for calculating the isobaric volume expansion with temperature by taking into account the volume dependence of the Anderson-Gruneisen parameter The calculations have been performed in the temperature range 298–1073 K along isobars in the pressure range 0–90 kbar. The results have been found to present good agreement with the experimental data available for the crystals under study.

**Keywords** : Thermal volume expansion, alkali halides, Anderson-Gruneisen parameter

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## 1. Introduction

Thermal expansivity of solids plays a significant role in understanding the thermodynamic and thermoelastic properties of solids under high pressure and high temperature [1–3]. An analysis of thermal expansivity of solids at simultaneously elevated pressure and temperature, can be presented by studying the expansion in volume due to rise in temperature along an isobar, *i.e.* at a constant pressure. The thermal expansivity or volume thermal expansion coefficient $\alpha$ for a material is defined as follows :

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P. \tag{1}$$

The volume dependence of $\alpha$ is related to the Anderson-Gruneisen parameter $\delta_T$ [4–6] given below

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{dK_T}{dT}\right)_P, \tag{2}$$

where $K_T$ is the isothermal bulk modulus. It has been observed experimentally that for solids, $\alpha$ increases with temperature, and $K_T$ decreases with increase in temperature such that the product $\alpha K_T$ remains nearly constant at high temperatures [1,7]. Thus, we can write

$$\left[\frac{d(\alpha K_T)}{dT}\right]_P = 0. \tag{3}$$

Eq. (3) yields

$$\left(\frac{dK_T}{dT}\right)_P = -\frac{K_T}{\alpha}\left(\frac{d\alpha}{dT}\right)_P. \tag{4}$$

Now using eqs. (1) and (4) in eq. (2), we get

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_P. \tag{5}$$

Assuming the Anderson-Grunеisen parameter to remain constant, we can integrate eq. (5) to obtain

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_T}, \tag{6}$$

where $\alpha_0$ and $V_0$ are the values at $T = T_0 = 298$ K. Eq. (6) was first obtained by Anderson [4] and has been discussed more recently in the literature [5,6]. Recent studies [8,9] have, however, revealed that $\delta_T$ does not remian constant but changes significantly with the change in volume. In the present study, we take into account the variation of $\delta_T$ with volume and obtain an expression for the isobaric volume expansion with the temperature. The method of analysis is given in Section 2. Results are discussed and compared with available experimental data in Section 3.

## 2. Method of analysis

The volume dependence of the Anderson-Grunеisen parameter $\delta_T$ can be expressed with the help of the following relationship [8,9]

$$\delta_T(T,P) + 1 = A\frac{V(T,P)}{V(T_0,P)}, \tag{7}$$

where $$A = \delta_T(T_0,P) + 1. \tag{8}$$

With the help of the relationship (7), we can rewrite eq. (5) as follows

$$\left[\delta_T(T_0,P) + 1\right]\frac{V(T,P)}{V(T_0,P)} - 1 = \frac{V(T,P)}{\alpha(T,P)}\left[\frac{d\alpha(T,P)}{dV(T,P)}\right]_P. \tag{9}$$

On integrating eq. (9), we get

$$\frac{\alpha(T,P)}{\alpha(T_0,P)} = \frac{V(T_0,P)}{V(T,P)}\exp\left[\left(\delta_T(T_0,P)+1\right)\times\left\{\frac{V(T,P)}{V(T_0,P)} - 1\right\}\right]. \tag{10}$$

Now taking $\alpha = (1/V)(dV/dT)_P$ in eq. (10) and integrating once again, we finally obtain

$$\frac{V(T,P)}{V(T_0,P)} = 1 - \frac{}{\left(\delta_T(T_0,P)+1\right)}$$

$$\ln\left\{1 - \alpha(T_0,P)\left(\delta_T(T_0,P) + 1\right) \times \left(T - T_0\right)\right\}. \tag{11}$$

It should be mentioned that eq. (11) is valid at all values of pressure $P$. It reduces to the equation reported by Kushwah *et. al.* [10] at $P = 0$ if we take $\delta_T(T_0,P) = \delta_{T_0}$. Thus eq. (11) obtained in the present study is an improvement over the equation reported by Kushwah *et. al.* [10] as we have taken into account the pressure dependence of $\delta_T$ along different isobars. Values of $\delta_T(T_0,P)$ which remain constant along a given isobar are obtained from the following relationship given by Chopelas and Boehler [8]

$$\delta_T(T_0,P) + 1 = \left[\delta_T(T_0,O) + 1\right]\frac{V(T_0,P)}{V(T_0,O)} \tag{12}$$

Eq. (12) has recently been used by Kumar [11,12] for investigating the thermodynamic behaviour of solids under high pressures. We have calculated the values of $\delta_T(T_0,P)$ from eq. (12) using the experimental data reported by Yagi [13]. Values of $\delta_T(T_0,P)$ thus obtained are given in Table 1 along with the input data.

### 3. Results and discussions

We have calculated $V(T,P)/V(T_0,P)$, the expansion of volume with temperature in the range 298–1073 K along isobars corresponding to the pressure range 0–90 kbar at an interval of 10 kbar for LiF, NaF and CsCl crystals. Values of input data given in Table 1 are used in eq. (11) to obtain the results reported in Table 2 and compared with the corresponding values obtained from the experimental data [13]. It is found that the values calculated from eq. (11) present close agreement with the experimental data for the entire range of temperature and pressure in case of all the three crystals under study. The isobaric volume expansions calculated in the present study, are related to the volumes $V(T,P)$ at simultaneously elevated pressures and temperatures by the following relationship

$$\frac{V(T,P)}{V(T_0,O)} = \frac{V(T_0,P)}{V(T_0,O)}\cdot\frac{V(T,P)}{V(T_0,P)}. \tag{13}$$

In eq. (13), the term $V(T_0,P)/V(T_0,O)$ represents the isothermal compression with pressure at $T = T_0$ and it can be determined with the help of an isothermal equation of state such as the Birch-Murnaghan equation of state [14]. However in the present study, we have concentrated on determining the isobaric expansion of volume with temperature along isobars, *i.e.* the change in volume from $V(T_0,P)$ to $V(T,P)$, at constant pressure $P$.

**Table 1.** Values of input data [10,13]

| P(kbar) | $\frac{V(T_0,P)}{V(T_0,O)}$ | $\delta(T_0,P)$ | $\alpha(T_0,P)$ $(10^{-4}K^{-1})$ | P(kbar) | $\frac{V(T_0,P)}{V(T_0,O)}$ | $\delta(T_0,P)$ | $\alpha(T_0,P)$ $(10^{-4}K^{-1})$ | P(kbar) | $\frac{V(T_0,P)}{V(T_0,O)}$ | $\delta(T_0,P)$ | $\alpha(T_0,P)$ $(10^{-4}K^{-1})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | LiF | | | | NaF | | | | CsCl | | |
| 0 | 1.0000 | 6.07 | 0.996 | 0 | 1.0000 | 5.84 | 0.959 | 0 | 1.0000 | 6.82 | 1.412 |
| 10 | 0.9854 | 5.97 | 0.948 | 10 | 0.9791 | 5.70 | 0.891 | 10 | 0.9526 | 6.45 | 1.091 |
| 20 | 0.9717 | 5.87 | 0.915 | 20 | 0.9605 | 5.57 | 0.858 | 20 | 0.9159 | 6.16 | 0.853 |
| 30 | 0.9589 | 5.78 | 0.894 | 30 | 0.9436 | 5.45 | 0.827 | 30 | 0.8860 | 5.93 | 0.690 |
| 40 | 0.9467 | 5.69 | 0.878 | 40 | 0.9283 | 5 35 | 0.806 | 40 | 0.8609 | 5.73 | 0.540 |
| 50 | 0.9352 | 5.61 | 0.857 | 50 | 0 9142 | 5.25 | 0.781 | 50 | 0.8391 | 5.56 | 0.440 |
| 60 | 0.9243 | 5.53 | 0.839 | 60 | 0.9012 | 5.16 | 0.761 | 60 | 0.8201 | 5.41 | 0.344 |
| 70 | 0.9140 | 5.46 | 0.823 | 70 | 0.8890 | 5.08 | 0.746 | 70 | 0.8031 | 5.28 | 0.270 |
| 80 | 0.9041 | 5.39 | 0.808 | 80 | 0.8777 | 5.00 | 0.732 | 80 | 0.7878 | 5.16 | 0.204 |
| 90 | 0.8946 | 5.32 | 0.794 | 90 | 0.8673 | 4.93 | 0.718 | 90 | 0.7739 | 5.05 | 0.150 |

Table 2. Values of $\frac{V(T,P)}{V(T_0,P)}$ the isobaric expansion of volume with temperature; (a) Calculated in the present study using eq. (11), and (b) experimental values [13].

| Temperature | LiF | | NaF | | CsCl | |
|---|---|---|---|---|---|---|
| (K) | (a) | (b) | (a) | (b) | (a) | (b) |
| | | | Pressure $P$ = 0 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0186 | – | 1.0178 | 1.0185 | 1.0275 | 1.0272 |
| 573 | 1.0304 | 1.0330 | 1.0291 | – | 1.0463 | – |
| 673 | 1.0434 | – | 1.0413 | 1.0419 | 1.0684 | 1.0647 |
| 873 | 1.0734 | 1.0814 | 1.0692 | 1.0685 | 1.1288 | 1.1090 |
| 1073 | 1.1116 | 1.1240 | 1.1038 | 1.1007 | 1.2476 | – |
| | | | Pressure $P$ = 10 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0176 | – | 1.0165 | 1.0179 | 1 0206 | 1.0196 |
| 573 | 1 0288 | 1.0316 | 1.0268 | – | 1.0340 | – |
| 673 | 1 0409 | – | 1 0378 | 1.0393 | 1.0488 | 1.0468 |
| 873 | 1.0686 | 1.0766 | 1.0628 | 1.0631 | 1 0846 | 1.0758 |
| 1073 | 1 1030 | 1.1155 | 1.0927 | 1.0925 | 1.1334 | – |

**Table 2.** *(Cont'd.)*

| Temperature | LiF | | NaF | | CsCl | |
|---|---|---|---|---|---|---|
| (K) | (a) | (b) | (a) | (b) | (a) | (b) |
| | | | Pressure $P$ = 20 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0170 | – | 1.0158 | 1.0170 | 1.0158 | 1.0148 |
| 573 | 1.0276 | 1.0303 | 1.0256 | – | 1.0257 | – |
| 673 | 1.0391 | – | 1.0361 | 1.0370 | 1.0363 | 1.0358 |
| 873 | 1.0653 | 1.0726 | 1.0596 | 1.0588 | 10.604 | 1.0567 |
| 1073 | 1.0972 | 1.1081 | 1.0874 | 1.0855 | 1.0896 | – |
| | | | Pressure $P$ = 30 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0165 | – | 1.0152 | 1.0161 | 1.0126 | 1.0114 |
| 573 | 1.0269 | 1 0288 | 1.0246 | – | 1.0203 | – |
| 673 | 1.0380 | – | 1.0346 | 1.0350 | 1.0285 | 1.0281 |
| 873 | 1.0632 | 1.0687 | 1.0568 | 1.0553 | 1.0464 | 1.0438 |
| 1073 | 1.0936 | 1.1013 | 1.0827 | 1.0796 | 1.0668 | – |

**Table 2.** *(Cont'd.)*

| Temperature | LiF | | NaF | | CsCl | |
|---|---|---|---|---|---|---|
| (K) | (a) | (b) | (a) | (b) | (a) | (b) |
| | | | Pressure $P$ = 40 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0162 | – | 1.0148 | 1.0151 | 1.0098 | 1.0087 |
| 573 | 1.0263 | 1.0276 | 1.0239 | – | 1.0156 | – |
| 673 | 1.0372 | – | 1.0336 | 1.0332 | 1.0218 | 1.0223 |
| 873 | 1.0616 | 1.0655 | 1.0549 | 1.0522 | 1.0348 | 1.0342 |
| 1073 | 1.0908 | 1.0952 | 1.0796 | 1.0742 | 1.0492 | – |
| | | | Pressure $P$ = 50 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0158 | – | 1.0143 | 1.0140 | 1.0079 | 1.0088 |
| 573 | 1.0256 | 1.0262 | 1.0231 | – | 1.0126 | – |
| 673 | 1.0361 | – | 1.0323 | 1.0315 | 1.0175 | 1.0179 |
| 873 | 1.0596 | 1.0624 | 1.0527 | 1.0497 | 1.0277 | 1.0269 |
| 1073 | 1.0875 | 1.0896 | 1.0760 | 1.0696 | 1.0386 | – |

**Table 2.** *(Cont'd.)*

| Temperature | LiF | | NaF | | CsCl | |
|---|---|---|---|---|---|---|
| (K) | (a) | (b) | (a) | (b) | (a) | (b) |
| | | | Pressure $P$ = 60 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0154 | – | 1.0139 | 1.0130 | 1.0061 | 1.0050 |
| 573 | 1.0250 | 1.0249 | 1.0224 | – | 1.0098 | – |
| 673 | 1.0352 | – | 1.0314 | 1.0300 | 1.0135 | 1.0141 |
| 873 | 1.0579 | 1.0597 | 1.0510 | 1.0474 | 1.0212 | 1.0209 |
| 1073 | 1.0846 | 1.0845 | 1.0733 | 1.0654 | 1.0292 | – |
| | | | Pressure $P$ = 70 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0151 | – | 1.0136 | 1.0120 | 1.0048 | 1.0036 |
| 573 | 1.0245 | 1.0235 | 1.0219 | – | 1.0076 | – |
| 673 | 1.0344 | – | 1.0307 | 1.0286 | 1.0105 | 1 0111 |
| 873 | 1.0565 | 1.0572 | 1.0497 | 1.0456 | 1.0163 | 1.0159 |
| 1073 | 1.0822 | 1.0798 | 1.0712 | 1.0616 | 1.0224 | – |

**Table 2.** *(Cont'd.)*

| Temperature | LiF | | NaF | | CsCl | |
|---|---|---|---|---|---|---|
| (K) | (a) | (b) | (a) | (b) | (a) | (b) |
| | | | Pressure $P$ = 80 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0148 | – | 1.0133 | 1.0109 | 1.0036 | 1.0024 |
| 573 | 1.0240 | 1.0223 | 1.0215 | – | 1.0057 | – |
| 673 | 1.0337 | – | 1.0300 | 1.0273 | 1.0078 | 1.0085 |
| 873 | 1.0551 | 1.0550 | 1.0485 | 1.0439 | 1.0122 | 1.0118 |
| 1073 | 1.0800 | 1.0753 | 1.0693 | 1.0581 | 1.0166 | – |
| | | | Pressure $P$ = 90 (kbar) | | | |
| 298 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 473 | 1.0145 | – | 1.0131 | 1.0097 | 1.0026 | 1.0012 |
| 573 | 1.0235 | 1.0211 | 1.0210 | – | 1.0042 | – |
| 673 | 1.0330 | – | 1.0293 | 1.0259 | 1.0057 | 1.0053 |
| 873 | 1.0539 | 1.0529 | 1.0474 | 1.0421 | 1.0089 | 1.0081 |
| 1073 | 1.0779 | 1.0713 | 1.0675 | 1.0547 | 1.0121 | – |

Eq. (11) obtained in the present study, represents an isobaric equation of state yielding the relationship between volume and temperature at constant pressure. At $T = T_0$, we have the initial boundary condition

$$\frac{V(T,P)}{V(T_0,P)} = 1 \tag{14}$$

which satisfies eq. (11).

We have thus demonstrated that eq. (11) can be used to predict the expansion in volume with the rise in temperature at $P = 0$ as well as at higher pressures along isobars with the help of input data at the initial temperature $T = T_0$ and at a pressure $P$ corresponding to each isobar. The results reported in Table 2 reveal that the rate of increase of volume with temperature becomes smaller at higher pressures. This is consistent with the prediction made earlier [1] that for solids the thermal expansivity decreases with pressure. On the other hand, at a given pressure the thermal expansivity is higher at higher temperatures. Thus for example, for a crystal under study, the change in volume in raising the temperature from 873 K to 1073 K is higher than the corresponding change in volume from 473 K to 673 K. These predictions are consistent with the experimental data on the temperature dependence and pressure dependence of thermal expansivity for solids [1,4,5,9].

Finally, it should be mentioned that the formulation developed in the present study is based on the assumption that the product of $\alpha K_T$ is independent of temperature along an isobar (eq. 3). Thus, the present method is applicable for solids for which this assumption holds good. The alkali halides are the example of such solids. For solids like MgO and CaO, the assumption (eq. 3) holds good only at temperatures higher than their Debye temperatures. The present formulation is therefore applicable for these solids only at higher temperatures. Recently, Anderson [15] has discussed the variation of $\alpha K_T$ with temperature in different types of solids. There are several solids including alkali halides for which the product $\alpha K_T$ does not change with temperature appreciably [15] and for such solids the present formulation is valid.

## 4. Conclusions

We have thus presented an analysis of the volume expansion with temperature for LiF, NaF and CsCl along isobars at high pressures. We have derived a relationship for calculating the isobaric volume expansion with temperature by taking into account the volume dependence of the Anderson-Gruneisen parameter $\delta_T$. The present formulation is based on the assumption that the product $\alpha K_T$ does not change with temperature. The present method is thus applicable for solids for which this assumption holds good. The results obtained for the isobaric volume expansion in case of LiF, NaF and CsCl have been found to present good agreement with the available experimental data [13].

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### References

[1] O L Anderson *Equations of State of Solids for Geophysics and Ceramic Science* (New York : Oxford University Press) (1995)

[2] S S Kushwah, P Kumar and J Shanker *Indian J. Phys.* **80A** 429 (1997)

[3] S S Kushwah and J Shanker *Physica* **B225** 283 (1996)

[4] O L Anderson *J. Geophys. Res.* **72** 3661 (1967)

[5] A Dhoble and M P Verma *Phys. Stat. Sol.* **B133** 491 (1986); **136** 497 (1986)

[6] J Shanker and M Kumar *Phys. Stat. Sol.* **B179** 351 (1993)

[7] J L Tallon *J. Phys. Chem. Solids* **41** 837 (1980)

[8] A Chopelas and R Boehler *Geophys. Res. Lett.* **19** 1983 (1992)

[9] O L Anderson, D G Isaak and H Oda *Rev. Geophys.* **30** 57 (1992)

[10] S S Kushwah, P Kumar and J Shanker *Physica* **B229** 85 (1996)

[11] M Kumar *Solid State Commun.* **92** 463 (1994)

[12] M Kumar *Indian J. Pure Appl. Phys.* **34** 76 (1996)

[13] T Yagi *J. Phys. Chem. Solids* **39** 563 (1978)

[14] F Birch *J. Geophys. Res.* **91** 4949 (1986)

[15] O L Anderson *J. Phys. Chem. Solids* **58** 335 (1997)